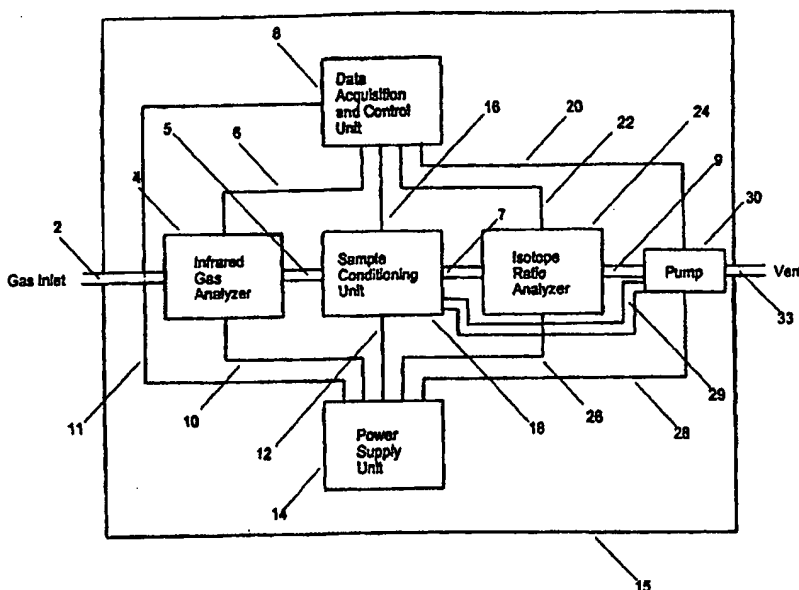




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(54) Title: APPARATUS AND METHOD FOR THE MEASUREMENT OF GLOBAL CARBON EMISSIONS FROM NATURAL AND ANTHROPOGENIC SOURCES



## (57) Abstract

The invention is an apparatus and method for precisely measuring concentration and isotope ratios of a component in a gas mixture. In one embodiment, the apparatus is designed to provide a portable and field deployable system capable of providing concentration and isotope ratio measurements in remote locations without physical intervention. In further embodiments, the apparatus is deployed to measure carbon dioxide in the atmosphere in order to determine the source of the carbon dioxide. An embodiment of the method includes measuring additional or different components of other gas mixtures.

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## **Apparatus and Method for the Measurement of Global Carbon Emissions from Natural and Anthropogenic Sources**

This application claims benefit of and priority from U.S. Provisional Application 60/075,338 filed February 20, 1998 and incorporated herein by reference.

### **Field of the Invention**

The present invention relates generally to the measurement of isotopes and more specifically to the quantitative and isotopic analysis of atmosphere gases, such as carbon dioxide (CO<sub>2</sub>), in order to determine and monitor global and regional carbon emissions from natural and anthropogenic sources.

### **Background of the Invention**

The apparatus and method described herein is based on the need for improved high-precision quantitative and isotope ratio measurements of key atmospheric species that are diagnostic of the functioning of planetary bio-geo-chemical cycles. The carbon cycle is an example of a bio-geo-chemical cycle of much debate and concern presently due to the addition of CO<sub>2</sub> from fossil fuel burning by humans. The need to monitor and track emissions of CO<sub>2</sub> from anthropogenic sources requires new instrumentation as the current approaches such as laboratory-based magnetic sector isotope ratio mass spectrometers are limited by their expense, size (making them unsuitable for deployment in the field) and difficulty of maintenance and particularly by their susceptibility to contaminants which requires extensive gas sample preparation. The goal of the invention described herein is to provide a low cost (relative to the current approaches), field ready, high-precision and simultaneous measurement of concentration and isotope ratio. The successful deployment of such systems will allow spatially resolved (e.g., local, state, region, country/nation and global levels), real time and high precision data to answer key questions underpinning market based policy decisions on greenhouse gas emissions according to the Kyoto Protocol (as further described below), as well as provide new data for multi disciplinary studies of global and regional climate change.

Although atmospheric CO<sub>2</sub> is used as an example here, any gas that can be generated and measured from any source is applicable, particularly soil gases, gases generated in closed spaces, experimental chambers, experimental apparatus or on other planetary surfaces. Some of these gases may include, but are not limited to:

5 methane, nitrous oxide, molecular oxygen, hydrogen and nitrogen, water vapor and carbon monoxide.

Continuing with the CO<sub>2</sub> example, there is immediate need for a method to monitor, track and verify the emissions of natural and anthropogenic sources of CO<sub>2</sub> to a degree well beyond the current technology which is based on magnetic

10 sector isotope ratio analysis. The emergence of a market-based trading system for carbon based on provisions of the Kyoto Protocol (FCCC 1997), specifically for atmospheric CO<sub>2</sub>, with its significant legal and economic consequences, presents a technically more demanding approach relative to studies of the global carbon cycle (see Tans *et al.*, *Global Change Biology* 2:309-318 (1996), incorporated herein by

15 reference). A device that had all the attributes described above would be very useful to track CO<sub>2</sub> emissions, or for that matter, all important greenhouse gases (methane, nitrous oxide and water vapor).

Again with respect to CO<sub>2</sub>, recognition of the vulnerability of the climate system to anthropogenic activity has resulted in international concern and a plan of

20 action to regulate emissions of carbon-based gasses. At a conference held December 1-11, 1997 in Kyoto, Japan, the parties to the U.N. Framework Convention on Climate Change agreed to an historic protocol to reduce greenhouse gas emissions by creating "carbon currency" tradable in the global marketplace to protect the environment. The Kyoto Protocol specified emissions targets and

25 timetables for industrialized nations and market-based measures for meeting those targets (see Anderson, J.W. 1998, *The Kyoto Protocol on Climate Change: Resources for the Future*, incorporated herein by reference). A central feature of the agreement is a set of binding emissions targets for developed nations which vary by country. Clearly, the need to develop credible approaches for quantifying

30 relevant carbon fluxes on a variety of spatial scales is critical and immediate for the implementation of the Kyoto Protocol. The invention described herein can address this need.

### Summary of the Invention

It is a goal of the present invention to provide a method and an apparatus for the precise measurement of the concentration and isotope ratios of a component in a gas mixture.

5        It is a further goal of the present invention to provide a portable instrument capable of simultaneous and precise measurement of the concentration and isotope ratios of a component in a gas mixture.

10       It is an additional goal of the present invention to provide a field deployable instrument capable of simultaneous and precise measurement of the concentration and isotope ratios of a component in a gas mixture.

It is also a goal of the present invention to provide an instrument that includes "universal" standard gas cells on which to base measurements and ensure comparable data across globally distributed analytical sites.

15       It is a further goal of the present invention to provide an instrument capable of multiple species analysis (i.e., for a variety of gases) and to provide such analysis in a non-destructive manner with respect to the sample.

It is an additional goal of the present invention to provide an instrument capable of being controlled and queried remotely as well as provide data in near real time via signal transmission.

20       It is a further goal to provide an instrument that can be expanded to include a variety of other sensors and sampling technologies as they become available.

25       The present invention is an apparatus and method for determining the concentration and the isotope ratio of a gas species present in a sample gas mixture. The system of the apparatus and method of the present invention may be used with a gas, liquid or solid sample, provided that the solid or liquid sample is first converted into a gas via heating, combustion or other suitable means.

30       The system utilizes a pump to draw the sample gas mixture into the system. The sample is next passed through a detector to measure the overall concentration of the desired species in question. The overall concentration of the desired species can be measured via an infrared gas analyzer or in any other fashion appropriate to the configuration and species being measured including a laser based device.

The sample is then optionally passed through a conditioner. The

conditioner performs one or more of the following operations: particle removal to clean the sample of particulate, component removal to remove one or more component gases from the sample (i.e., components that may interfere with later processing and detection), concentration of the desired species, and addition of a carrier to facilitate processing. In particularly harsh environments, particle filtration may be applied at an earlier position in the sample path.

The system passes the sample to the isotope ratio analyzer. The analyzer detects the concentration of a predetermined isotope of the desired species. The analyzer may be any conventional isotope analyzer, but in a preferred embodiment the analyzer is a small and accurate laser based unit. For instance, a laser tuned to emit radiation at a wavelength appropriate for the predetermined isotope of the desired species can be used to excite the isotope species into an excited state. Simultaneously, the laser excites a known standard of the isotope species. An optogalvanic detector can be used to measure the level of excitation of both the sample and the standard and thus detect the concentration of the isotope. The isotope ratio is calculated by comparing the isotopic species concentration to the total species concentration measured earlier in the path.

In further embodiments of the invention, one or more detectors, conditioners and isotope analyzers can be combined allowing the measurement of multiple isotope ratios within the sample. They may be configured in a variety of system architectures, with some units operated serially and others operated in parallel.

In still other embodiments, the system is controlled by a microprocessor-based data acquisition and control unit, such as a personal computer. The data acquisition and control unit controls the operation of each portion of the system, collects measurements, performs data processing and data summary, stores the data and transmits the data. The data acquisition and control unit may also be connected to external sensors so as to monitor conditions external to the system (i.e., weather conditions including temperature, wind direction, wind speed, pressure and humidity, locational information such latitude and longitude via a global positioning system, and for water based units water temperature and salinity) and internal to the system (i.e., power condition, temperature, system functionality etc.) All of the information may be transmitted via a radio transmitter to a central

base station that can collect the data, monitor system operations and monitor external conditions. The base station may optionally transmit new programs into the system when the system is configured with a receiver connected to the computer.

5           The system is designed to be modular, portable and self contained. The system can utilize conventional line power but can also utilize batteries. If batteries are utilized, the system can also charge the batteries via a solar cell array, thus allowing remote operation. The system is contained in a weather proof housing that also provides the platform for external sensors, radio antennae and solar cell  
10           arrays. In a preferred embodiment, the system can be utilized to measure and track the source of carbon dioxide in the environment.

          The above mentioned objectives of the present invention will become more apparent and the invention itself better understood with reference to the following description of the embodiments of the present invention in conjunction with the  
15           accompanying figures.

#### **Brief Description of the Figures**

          The foregoing discussion will be understood more readily from the following detailed description of the invention, when taken in conjunction with the  
20           accompanying drawings, in which:

          Fig. 1 is a block diagrammatic view of a preferred embodiment of the invention apparatus;

          Fig. 2 is a block diagrammatic view of an embodiment of a sample conditioning unit as incorporated in the apparatus of Fig. 1;

25           Fig. 3 is a block diagrammatic view of another embodiment of the sample conditioning unit as incorporated in the apparatus of Fig. 1, such sample conditioning unit utilizing a gas selective membrane;

          Fig. 4 is a block diagrammatic view of an embodiment of the sample conditioning unit as incorporated in the apparatus of Fig. 1, such sample  
30           conditioning unit utilizing a cryogenic trap;

          Fig. 5 is a schematic cross-sectional view of an embodiment of a cryogenic trap as incorporated in the sample conditioning unit of Fig. 4.

## Reference numerals in the Figs.:

	2	gas-tight inlet tube
	4	infrared gas analyzer
	5	gas-tight coupling tube
5	6	electrical connection
	7	gas-tight coupling tube
	8	microprocessor-based data acquisition unit
	9	gas-tight coupling tube
	10	electrical connection
10	11	electrical connection
	12	electrical connection
	14	self contained power supply unit
	15	weather hardened container
	16	electrical connection
15	18	sample conditioning unit
	20	electrical connection
	22	electrical connection
	24	isotope ratio analyzer
	26	electrical connection
20	28	electrical connection
	29	coupling tube
	30	diaphragm pump
	33	vent tube
	34	gas inlet tube
25	36	oxygen scrubber
	38	gas outlet tube
	40	gas inlet tube
	42	gas-tight gas chamber
	44	gas-tight coupling tube
30	46	gas selective membrane
	48	gas-tight coupling tube tee
	50	pure nitrogen source
	52	gas-tight coupling
	54	flow controlling valve
35	56	gas outlet tube
	58	gas-tight coupling tube
	60	vacuum compatible solenoid valve
	62	gas-tight coupling tube
	64	gas-tight inlet tube
40	66	vacuum compatible solenoid valve
	68	gas-tight coupling tube tee
	70	gas-tight coupling tube
	72	solenoid valve
	74	pure nitrogen source
45	76	four-port, two position flow switching valve
	78	coupling tube
	80	coupling tube



	82	cryogenic trap
	84	gas outlet tube
	86	coupling tube
	88	stainless steel lid
5	90	disc
	92	gas-tight electrical feed-through
	94	open end of 'U' tube
	98	open end of 'U' tube
	100	stainless steel vent tube
10	102	solenoid valve
	104	gas exhaust tube
	106	fiberglass-insulated resistance heating wire
	108	stainless steel 'U' tube
	110	stainless steel cylinder
15	112	liquid nitrogen dewar

### Detailed Description of Preferred Embodiments

A preferred embodiment of the invention is shown diagrammatically in Fig.

1. The invention comprises a gas-tight gas inlet tube 2 connected to the input of an infrared gas analyzer ("IRGA") 4 such as model LI-6251 sold by LI-COR, Inc. of Lincoln, NE. The gas outlet of the IRGA 4 is connected to the inlet of a sample conditioning unit 18 by a gas-tight coupling tube 5. A description of some of the possible embodiments of the sample conditioning unit 18 apparatus are included below. The sample conditioning unit 18 is in turn connected by a gas-tight coupling tube 7 to an isotope ratio analyzer 24, such as the LARA™ sold by Diagnostics and Devices, Inc. of Morris Plains, NJ. The gas outlet of the isotope ratio analyzer 24 is in turn connected by another gas-tight coupling tube 9 to the inlet of a diaphragm pump 30 such as the Air Cadet® models sold by Cole Parmer Instrument Company of Vernon Hills, IL. The gas outlet of pump 30 is connected to a vent tube 33 which is also gas-tight and is directed away from gas inlet tube 2. One of the possible embodiments of the sample conditioning unit apparatus 18 requires a gas-tight coupling tube 29 to be connected from a second gas outlet of the sample conditioning unit 18 to the inlet of the pump 30. The gas-tight tubing used for the gas inlet tube 2, coupling tubes 5, 7, 9, and vent tube 33 is preferably at least 1/8 inch internal diameter and is made from a material such as stainless steel or PEEK.

A preferred embodiment of the invention employs a microprocessor-based

data acquisition and control unit 8 capable of acquiring and storing the data generated by the IRGA 4 and the isotope ratio analyzer 24. The data acquisition and control unit must also be capable of controlling the operation of the pump 30 and the operation of the valves employed in the sample conditioning unit. Fig. 1  
5 shows the electrical connections 6, 16, 22, 20 from the data acquisition and control unit 8 to the IRGA 4, sample conditioning unit 18, isotope ratio analyzer 24 and the pump 30, respectively.

If the current invention is deployed remotely, then the data acquisition and control unit 8 is also capable of controlling and acquiring data from additional  
10 sensors which may be used to monitor prevailing weather conditions, for example. If the current invention is deployed remotely, the data acquisition and control unit 8 can be fitted with a satellite communication system to transmit collected data on a periodic basis. The system is also field programmable, allowing the system to be reconfigured to control additional instruments, conduct additional experiments and  
15 calculate new intermediate values. When equipped with a receiver, the system can also download configuration information, tests and additional program control.

A personal computer fitted with an interface board to allow valve control and analog to digital converters to allow acquisition could also be used. There are many suppliers of suitable interface boards such as National Instruments, Austin,  
20 TX 78730. The computer is also used to gather and store the measurement data and, if the system is remotely deployed, transmit the data to some control center. A remotely deployed system could also receive information from the control center, such as calibration information, measurement schedules, and other instructions. The computer may also accept data provided by additional sensors such as those  
25 capable of sensing current weather conditions or other factors which may influence the measurement or sampling conditions. If the system is field deployed and is being powered by batteries, generators or rechargers of some sort, the personal computer can also be used to monitor, control and optimize power usage.

A power supply unit 14 is utilized to provide power through electrical  
30 connections 11, 10, 12, 26, 28 to the data acquisition and control unit 8, IRGA 4, sample conditioning unit 18, isotope ratio analyzer 24 and the pump 30, respectively. In one embodiment of the invention, the system would be self-

contained, portable and field deployable. This embodiment would require that the power supply unit 14 comprise of any combination of battery, generator or recharging device such that the total power requirements of the instrument be met for the required period of operation. For example, a bank of rechargeable batteries  
5 could be used to provide power for the instruments, while one or more photovoltaic arrays are used to recharge the batteries during daylight periods. Alternatively, batteries could be used to power the data acquisition and control unit 8 during dormant periods (when analyses are not required) and when an analysis is required, a portable gas-powered generator could be started automatically (by the data  
10 acquisition and control unit 8) in order to provide for the higher power demands of the instrumentation. When the analysis cycle is complete, the generator is automatically switched off and battery-powered dormancy resumes.

Figs. 2, 3 and 4 show three of numerous possible embodiments of the sample conditioning unit 18. Fig. 2 shows the simplest of the three possibilities  
15 and comprises a gas inlet tube 34 (which is connected to the coupling tube 5 in Fig. 1), an oxygen scrubber 36 such as Oxy-Trap™ sold by Alltech Associates of Deerfield, IL, and a gas outlet tube 38 (which is connected to coupling tube 7 in Fig. 1). The variation of the oxygen scrubber 36 sold by Alltech Associates is of the chemical scrubber type, of course the oxygen scrubber may also comprise a  
20 simple canister or other container filled with any oxygen absorbent, as is known in the art. Furthermore, the scrubber 36 could be further modified to remove gases other than or in addition to oxygen. The gas inlet tube 34 and gas outlet tube 38 are of the same material and dimensions as the gas-tight tubing used for coupling tubes 5, 7, 9 described previously.

Fig. 3 depicts an alternative embodiment of the sample conditioning unit 18  
25 which includes a gas chamber 42, a gas selective membrane 46 and a carrier gas source 50. A gas inlet tube 40 (which is connected to the coupling tube 5 of Fig. 1) is connected to the gas-tight gas chamber 42 which has a volume sufficient to contain a sample for analysis, preferably at least 500 ml. The gas chamber 42 has  
30 two outlet ports, one of which is connected to a gas-tight coupling tube 44 which in turn is connected to the inlet of the gas selective membrane 46. The second outlet port of the gas chamber 42 is connected to another gas-tight coupling tube 58

which at its other end is connected to the inlet port of a vacuum-compatible solenoid valve 60 such as the Model 52 sold by Peter Paul Electronics Co., Inc. of New Britain, CT. The outlet port of solenoid valve 60 is connected to a gas-tight coupling tube 62. Gas-tight coupling tube 62 connects to the coupling tube 29  
5 shown in Fig. 1 which ultimately connects to the gas inlet of the pump 30 also shown in Fig. 1. The coupling tube 58, solenoid valve 60 and coupling tube 62 are schematically depicted in Fig. 1 as the second gas-tight coupling tube 29 connected between the sample conditioning 18 unit and the pump 30.

Turning back to Fig. 3, the outlet of the gas selective membrane 46 is  
10 connected to another gas-tight coupling tube tee 48. The coupling tube tee 48 is connected to a gas outlet tube 56 (which is connected to the coupling tube 7 of Fig. 1) and is also connected to the outlet of a flow controlling valve 54 such as the Series 810 sold by Sierra Instruments, Inc. of Monterey, CA 93940. The inlet of the flow controlling valve 54 is connected via a gas-tight coupling tube 52 to the  
15 carrier gas source 50. In a preferred embodiment of the present invention, the carrier gas source can be any suitable gas such as pure nitrogen gas in a high-pressure cylinder or from a pure nitrogen generator such as those sold by Nitrotec, Inc. of Linthicum, MD. The gas inlet tube 40, coupling tubes 44, 58, 62, 52, coupling tube tee 48, and the gas outlet tube 56 are all preferably of the same  
20 dimensions and material as the gas-tight tubing used for coupling tubes 5, 7, 9 described previously.

Fig. 4 shows another preferred embodiment of the sample conditioning unit apparatus 18. A gas-tight gas inlet tube 64 (which is connected to the coupling tube 5 of Fig. 1) is connected to the inlet port of a vacuum-compatible solenoid  
25 valve 66 which is comparable in design to solenoid valve 60 described previously. The outlet port of solenoid valve 66 is connected to a gas-tight coupling tube tee 68. The coupling tube tee 68 is connected at its other ends to the inlet of a cryogenic trap 82 and to a carrier gas source 74 via a flow-controlling valve 72 and a gas-tight coupling tube 70. Again, the carrier gas source can be any suitable gas  
30 including pure nitrogen gas in a high-pressure cylinder or from a pure nitrogen generator as sold by Nitrotec, Inc. of Linthicum, MD. The outlet of the cryogenic trap 82 is connected to a gas outlet tube 84. Inlet tube 64, coupling tube tee 68,

coupling tube 70 and outlet tube 84 are all preferably of similar dimensions and material as the gas-tight tubing used for coupling tubes 5, 7, 9 described previously.

Fig. 5 depicts a preferred embodiment of the cryogenic trap apparatus 82 shown in Fig. 4. The cryogenic trap apparatus 82 comprises a stainless steel cylinder 110 which is approximately 6 inches long having an approximately 1 inch internal diameter. The cylinder 110 is closed at its upper end by a stainless steel disc 90 which is welded to the top edge of the cylinder 110 to form a gas-tight seal. The disc 90 has holes drilled in it through which the ends of a stainless steel 'U' tube 108 are passed and welded to form gas-tight seals. The welding of the 'U' tube 108 to the disc 90 does not obstruct gas passage through the internal diameter of the tube and also supports the tube firmly in place. The 'U' tube 108 preferably has an internal diameter of at least 1/16 of an inch and protrudes at least 2 inches above the disc 90. The disc 90 houses two gas-tight electrical feed-thrus 92 which allow electrical connection to the fiberglass-insulated resistance heating wire 106. The heating wire 106 is tightly wrapped around the 'U' tube 108 in order to be in good thermal contact with it. The disc 90 has one more hole drilled through it and a 1/8 inch internal diameter stainless steel vent tube 100 is pushed through and welded in place in the same manner as the 'U' tube 108. The disc 90 then has only one gas escape path and that it through stainless steel vent tube 100. The vent tube 100 is connected to the inlet of a solenoid valve 102 of similar specification and design as the Peter Paul model 52 described previously. The outlet of the solenoid valve 102 is connected to a gas exhaust tube 104. A liquid nitrogen dewar 112 has an internal diameter of approximately 6 inches, is approximately 8 inches deep and has a stainless steel lid 88. The dewar's steel lid 88 supports the cylinder 110 and attached components. The dewar's lid 88 has a hole drilled in its center which is large enough to allow cylinder 110 to snugly fit into it. Approximately 1/4 inches from the top edge of the cylinder 110, the lid is tack-welded in order to hold the cylinder firmly in place. With the dewar lid 88 in place on the dewar 112, the cylinder and attached components are firmly held in place in the middle of the dewar 112 and at least 1/2 inch off the bottom of the dewar 112. The 'U' tube 108 has open ends 94 and 98 protruding above the disc

90 such that connections can be made to coupling tee 68 and coupling tube 84 shown in Fig. 4.

Now that the details of a preferred embodiment of the cryogenic trap 82 (depicted schematically in Fig. 4) have been described with respect to Fig. 5, it should be noted that the ports of the flow-switching valve 76 shown in Fig. 4 are configured in such a way as to provide a gas flow path straight from coupling tube 86 through to gas outlet tube 84 when in one position and a gas flow path from coupling tube 86, through the cryogenic trap 82 and then to the gas outlet tube 84 to trap in a gas when in a second position.

It also should be noted that the gas inlet tubes of each of the sample conditioning unit 18 shown in Figs. 2, 3 and 4, are connected via coupling tube 5 shown in Fig. 1 to the outlet of the IRGA 4. Similarly, the gas outlet tubes from each of the three embodiments of the sample conditioning unit 18 shown in Figs. 2, 3 and 4 are connected via coupling tube 7 shown in Fig. 1 to the inlet of the isotope ratio analyzer 24.

The components of the present invention are preferably housed or mounted in a weather-hardened container 15 (see Fig. 1), especially if the invention is field deployed. Such a container would protect the components from damage and also provide a platform for mounting additional sensors, photovoltaic arrays and antenna, if necessary. If the design incorporates external sensors, then the data from the sensors would also be collected by the data acquisition and control unit 8.

#### General Operation

In a preferred embodiment of the invention, measurement of a species concentration and the isotope ratios of the species (i.e., carbon dioxide concentration and carbon isotope ratios) of a gas mixture, such as air, is performed. With reference to Fig. 1, the system operates as follows. The gas sample is input via gas inlet tube 2 into the system. In further embodiments of the invention, the inlet tube 2 may be connected to a combustion chamber to provide a gaseous sample of a solid. Such a combustion chamber can be formed utilizing a thermo-electric heating element in a chamber holding the sample or can utilize a conventional combustion chamber used in mass spectrometer.

The gas sample is pulled into and through the system via operation of pump 30. Initially a measurement of the total concentration of the subject gases is conducted. In an embodiment of the present invention for measuring carbon isotopes, IRGA 4 provides the total CO<sub>2</sub> concentration of the input sample without the need for any kind of preprocessing or conditioning. In additional embodiments of the invention targeted for harsh environments, a conditioning unit may be added to remove moisture, dust etc. This can be accomplished by filter units utilizing selective membranes to remove unwanted constituents as known in the art or utilizing chemical scrubbers as is known in the art.

The system then passes the constituent gases to one or more optional conditioning units to remove certain constituent gases and/or to concentrate the gas or gases of interest. For instance, in the embodiment of the invention for determining the concentration of carbon isotopes, isotope ratio analyzer 24 is capable of providing the carbon isotope ratios, but is subject to interference by the presence of oxygen within the sample. Therefore in the previously discussed embodiments (as depicted in Figs. 2, 3 and 4), the sample conditioning unit 18 can remove oxygen from the sample gas before it enters the isotope ratio analyzer 24. The precision of the measurement provided by the isotope ratio analyzer 24 can be further improved by increasing the concentration of the desired species within the sample. For the embodiments directed to CO<sub>2</sub> detection, concentration is preferably increased to 1% or more by volume. In addition, the precision can be improved by supplying an inert carrier into the sample stream. Again, with reference to a CO<sub>2</sub> unit, the sample containing 1% CO<sub>2</sub>, is mixed with pure nitrogen or another inert and non-interfering carrier gas. Therefore, the isotope ratio measurements provided by the isotope ratio analyzer 24 can be optimized by a sample conditioning unit 18 by concentrating the particular specie or species in the subject gas sample and by mixing it or them with a carrier gas.

The input sample is next passed to one or more isotope analyzers to detect the various isotopes of the subject gases in the sample. The isotope ratio analyzer can utilize any device for measuring the isotopic composition of a gas, but in a preferred embodiment the system utilizes a low mass, low power, compact device. For a system measuring carbon isotopes, one such carbon 13 isotope analyzer is

taught in U.S. Patent No. 5,394,236. In additional embodiments of the present invention, for instance an embodiment for detecting carbon 14, the system utilizes a coherent light source emitting energy to resonate selectively for desired subject gas. For example, measuring isotopic carbon 14 would utilize a  $^{14}\text{CO}_2$  isotopic laser for radiating the sample and a known standard correlation cell containing the subject gas, here carbon 14. The ratio measurements may thus be conducted in a manner as taught in U.S. Patent No. 5,394,236, the teachings of which are incorporated herein by reference. Once all analysis is complete, the sample gases are evacuated from the system into the environment, preferably in direction away from the input area.

Variations of the basic system are available. For instance, an expansion upon the basic system is possible by combining a number of the basic building blocks into a single unit to detect additional species and isotopes. In this case, a number of isotope ratio analyzers 24 are utilized. Each analyzer 24 would detect the presence of an isotopic species in the sample. Because the system does not consume the sample during detection, it is possible to sequentially arrange a number of detectors to receive the sample over time. Each ratio analyzer 24 could optionally include a conditioning unit to condition the sample prior to isotopic measurements. In this series configuration, care must be given to ensure that conditioning units do not remove desired subject gases prior to analysis. An alternative architecture is to utilize a splitter to send a portion of the sample to each analyzer in parallel, thus allowing the ratio analyzers to operate independently. In either configuration, each analyzer could be operated selectively (i.e., only measure certain isotopic samples at certain times to reduce power consumption).

The system is designed to operate in remote locations, and monitor additional external conditions (i.e., temperature, humidity, wind direction, time, general weather conditions, etc) via conventional sensors mounted externally to the system. The complete unit is under the control of data acquisition and control unit 8.

### Example Operation of a Carbon 13 Analyzer

The  $^{13}\text{C}$  and  $^{14}\text{C}$  concentrations in atmospheric  $\text{CO}_2$  are required for a full deconvolution of natural and anthropogenic (e.g., fossil fuel) sources thereby



providing a basis for tradable CO<sub>2</sub> permits. In the case of CO<sub>2</sub>, a preferred embodiment of the proposed device is based on a laser (e.g., Laser Based Isotope Ratio Spectrometry, "LB-IRS"), for the determination of the carbon isotope ratios (<sup>13</sup>C, <sup>14</sup>C) of atmospheric CO<sub>2</sub>. In this system, the concentration may determined  
5 by either the laser or by an IRGA. The LB-IRS system for measuring the isotopic composition of atmospheric CO<sub>2</sub> in conjunction with high precision measurements of the concentration of CO<sub>2</sub> using laser gas analyzer technology as performed in the present invention provides a platform for the study of the global biosphere. An important aspect of this approach is the analysis of key isotopic species.

10 The laser-based approach of the present invention relies on optical stimulation of <sup>13</sup>CO<sub>2</sub> and <sup>12</sup>CO<sub>2</sub> species in a sample chamber by wavelength specific lasers. This technique achieves specificity to isotopic chemical species via the use of the optogalvanic effect ("OGE"). The OGE can be measured with very high signal to noise background ratios, and is proportional to laser power and is  
15 integrated over the discharge volume (see, for example, Murnick, D. and B.J. Peer, *Science* 263:945-947 (1994), incorporated herein by reference) and yield precision similar to that of the traditional mass spectrometers. The discharge is converted into an electrical signal and processed for a specified period of time, relative to a sealed standard gas chamber, depending on the required precision. Long  
20 measurement intervals, in principle, will exceed the precision typical of traditional isotope ratio mass spectrometers (i.e., < 0.01 per mil). Advantages of OGE can be understood from the following equation (see Murnick and Peer, *Science* 263:945-947 (1994)):

25 
$$S = nLI(\nu) A \sigma(\nu) C \quad (1)$$

where the electrical response,  $S$ , of the system with laser of average intensity ( $\text{Wcm}^{-2}$ )  $I$  and frequency  $\nu$  is incident on a weak electrical discharge,  $n$  is the density of interaction species,  $L$  is the length of the interaction region,  $\sigma$  defines the  
30 laser-species interaction cross section and  $C$  is an optogalvanic proportionality constant. Note that, according to (1) the signal is linear in both density  $n$  and laser power  $I$ . Increases in laser power provides for increased gain offering enhancement

of signals for dilute or very low concentration of isotopes relative to the majority species. Optimization of signals by varying gas mixtures, gas pressure and discharge power are possible and affect the parameter *C*. Unlike absorption and fluorescence measurements dependent on optical elements, OGE eliminates  
5 collection and dispersion optics and light transducers. Small discharge variations are canceled out by simultaneous measurement; the use of sealed working reference gases (resulting in long life) promises to eliminate instrument drift, off-sets between batches of standards prepared often (as is the case for traditional mass spectrometry) and differences between laboratories which are significant for the  
10 current flask sampling programs. Remotely operated units could process samples for as long as one hour intervals throughout the day to achieve high precision for measurement of atmospheric CO<sub>2</sub> isotope ratios (i.e., < 0.005 per mill (‰)) or for as short as 100 seconds (yielding precision for <sup>13</sup>C and <sup>18</sup>O of at least 0.01 and 0.1 per mill, respectively) for use in fast analytical schemes for plant physiological or  
15 biological monitoring. Samples can be analyzed in a semi-continuous batch mode or in continuous flow mode; each configuration may require different hardware, as described in the embodiments previously. In particular, in the present invention, as used in the case of CO<sub>2</sub>, could employ two isotopic lasers, one to determine the <sup>13</sup>C/<sup>12</sup>C ratios and an additional one to determine the <sup>14</sup>C/<sup>12</sup>C ratio (see, for example,  
20 Freed, C., *The Lincoln Laboratory Journal* Vol. 3, No. 3, 479-498 (1990), incorporated herein by reference).

A further application of a laser-based isotopic analysis of a gas (including analysis using LARA and/or LB-IRS) is the determination of the concentration of the species for which isotopic composition is also to be determined. The use of  
25 standard cells of known concentration and pressure and conditioning of the gas entering into the sample cell will allow determination of both concentration and isotopic composition. The benefit of such operation is the fact that a stand-alone second device for determination of concentration (e.g., an IRGA) would not be needed.

30

#### Specific Operation

The operation of the instrument for this example is as follows. With

reference to Fig. 1, under the control of the data acquisition and control unit 8, power is applied from power supply unit 14 to pump 30. Since the IRGA 4, sample conditioning unit 18, isotope ratio analyzer 24 and the pump 30 are all connected with coupling tubes 5, 7, 9 in order to provide a continuous gas flow path, gas present at gas inlet tube 2 is drawn through all of the tubing-coupled components and out of vent tube 33. After gas has passed through the IRGA 4, it passes through the sample conditioning unit 18 before entering the isotope ratio analyzer 24. As the gas is drawn through the oxygen scrubber 36 (as shown in Fig. 2), which constitutes the sample conditioning unit 18 in this preferred embodiment, oxygen is removed. The oxygen-free gas continues to be drawn through coupling tube 7 and into the isotope ratio analyzer 24. After sufficient gas has been drawn through the isotope ratio analyzer 24 to purge out any residual gas from a previous measurement, the data acquisition and control unit 8 stops the pump 30. Now that both the IRGA 4 and the isotope ratio analyzer 24 have received appropriate aliquots of the gas drawn in from the gas inlet tube 2, the data acquisition and control unit 8 initiates a concentration measurement of CO<sub>2</sub> by the IRGA 4 and an isotopic measurement of CO<sub>2</sub> by the isotope ratio analyzer 24. Measurement data generated by the IRGA 4 and isotope ratio analyzer is acquired and stored or transmitted by the data acquisition unit 8. The whole sequence of events can be repeated either immediately, or after a delay period as dictated by the program loaded into the data acquisition unit 8.

Operation of the present preferred embodiment of the invention with the sample conditioning unit 18 comprising the apparatus shown in Fig. 3 is as follows. Initially, solenoid valve 60 and flow-controlling valve 54 are closed allowing no gas to flow through them. Under the control of the data acquisition and control unit 8 (see Fig. 1), the solenoid valve 60 is opened and power is applied from power supply unit 14 (see Fig. 1) to pump 30 (see Fig. 1). Gas present at gas inlet tube 2 (see Fig. 1) is drawn into and through the IRGA 4 (see Fig. 1), through the coupling tube 5 (see Fig. 1), through the gas inlet tube 40, through the gas chamber 42 and through the solenoid valve 60. The gas continues to be drawn through coupling tube 62, coupling tube 29 (see Fig 1), pump 30 (see Fig 1) and finally out of the vent tube 33 (see Fig. 1). The gas selective membrane 46 provides

considerable resistance to the gas flow and so does not allow a significant amount of sample gas to pass through it during this stage of operation. When enough gas has been drawn through the IRGA 4 (see Fig. 1) and the gas chamber 42 to purge any gas remaining from previous measurements, the data acquisition and control unit 8 (see Fig. 1) closes solenoid valve 60. Since the IRGA 4 (see Fig. 1) has received a suitable aliquot of sample gas, the acquisition and control unit 8 (see Fig. 1) initiates a CO<sub>2</sub> concentration measurement. The pump 30 (see Fig. 1) continues to run and establishes vacuum conditions in the isotope ratio analyzer 24 (see Fig. 1), coupling tubes 7, 9, 29 (see Fig. 1), gas outlet tube 56, and coupling tube tee 48. When the pump 30 (see Fig. 1) has run long enough to achieve the desired vacuum in the attached components, the acquisition and control unit 8 (see Fig. 1) stops the pump 30 (see Fig. 1). The CO<sub>2</sub> in the sample gas contained in the gas chamber 42 now permeates the gas selective membrane 46 due to the pressure difference across it.

The CO<sub>2</sub> in the sample gas contained in gas chamber 42 is allowed to permeate the gas selective membrane until enough CO<sub>2</sub> has accumulated in the evacuated components to provide precise isotope ratio measurement when mixed with an appropriate amount of carrier gas, preferably pure nitrogen gas. Under the control of the data acquisition and control unit 8 (see Fig. 1), the flow-controlling valve 54 is opened enough to allow a charge of pure nitrogen gas to flow from the carrier gas source 50, through coupling tube 52. The nitrogen passes through coupling tube tee 48, through gas outlet tube 56, through coupling tube 7 (see Fig. 1) and into the isotope ratio analyzer 24 (see Fig. 1). Most of the CO<sub>2</sub> which had previously permeated the gas selective membrane 46 Fig. 3 is carried by the nitrogen gas flow into the isotope ratio analyzer 24 (see Fig. 1). The flow-controlling valve 54 is closed by the data acquisition and control unit 8 (see Fig. 1) when an optimal charge of gas is present in the isotope ratio analyzer 24 (see Fig. 1). At this time, the data acquisition and control unit 8 (see Fig. 1) initiates an isotope measurement of the CO<sub>2</sub> in the isotope ratio analyzer 24 (see Fig. 1). Measurement data generated by the IRGA 4 (see Fig. 1) and isotope ratio analyzer 24 (see Fig. 1) is acquired and stored or transmitted by the data acquisition unit 8 (see Fig. 1). The whole sequence of events can be repeated either immediately, or

after a delay period as dictated by the program loaded into the data acquisition unit 8 (see Fig. 1).

Operation of another preferred embodiment of the invention with the sample conditioning unit 18 comprising the apparatus shown in Fig. 4 is as follows.

5 Initially, solenoid valve 66 and flow-controlling valve 72 are closed allowing no gas to flow through them. Under the control of the data acquisition and control unit 8 (see Fig. 1), the solenoid valve 66 is opened and power is applied from power supply unit 14 (see Fig. 1) to pump 30 (see Fig.1). The data acquisition and control unit 8 (see Fig. 1) also sets the cryogenic trap 82 into the non-trapping state  
10 so that gas can flow freely through the cryogenic trap.

Next, gas present at gas inlet tube 2 (see Fig.1) is drawn into and through the IRGA 4 (see Fig. 1), through the coupling tube 5, through the gas inlet tube 64 and through the solenoid valve 66. The gas is then drawn through coupling tube tee 68 , cryogenic trap 82 and through the gas outlet tube 84. The gas flow then  
15 continues through the coupling tube 7 (see Fig. 1), isotope ratio analyzer 24 (see Fig. 1), coupling tube 9 (see Fig. 1), pump 30 (see Fig. 1), and out through the vent tube 33 (see Fig. 1). When enough gas has been drawn through the cryogenic trap 82 to purge any gas remaining from a previous measurement, the data acquisition and control unit 8 (see Fig. 1) sets the cryogenic trap 82 into the  
20 trapping mode. Gas continues to flow from the gas inlet tube 2 (see Fig. 1) all the way through the tubing-coupled components while condensable gas components are cryogenically trapped in the cryogenic trap 82. When gas has been flowing for a long enough time to allow an appropriate quantity of CO<sub>2</sub> to accumulate in the cryogenic trap 82, the data acquisition and control unit 8 (see Fig. 1) closes  
25 solenoid valve 66 and allows the pump 30 (see Fig. 1) to establish vacuum conditions in the coupling tube tee 68, cryogenic trap 82, outlet tube 84, coupling tubes 7 and 9 (see Fig. 1) and isotope ratio analyzer 24 (see Fig. 1). The data acquisition and control unit 8 (see Fig. 1) now initiates a concentration measurement on the aliquot of gas contained within the IRGA 4 (see Fig. 1).  
30 When the pump 30 (see Fig. 1) has continued to run for long enough to achieved its ultimate vacuum in the attached components, the acquisition and control unit 8 (see Fig. 1) stops the pump 30 (see Fig. 1) and sets the cryogenic trap 82 back to

its non-trapping state in order to release the trapped gas. As the gas is released from the cryogenic trap 82, it expands throughout the components previously under vacuum. When enough time has expired to allow the trapped sample to completely evaporate, the data acquisition and control unit 8 opens the flow-controlling valve 72 to allow the carrier gas, preferably pure nitrogen, from the carrier gas source 74 to flow through it. The nitrogen gas flows from the flow-controlling valve 72, through coupling tube tee 68, through the cryogenic trap 82, and out through the outlet pipe 84. The nitrogen flows through coupling tube 7 (see Fig. 1) and into the isotope ratio analyzer 24 (see Fig. 1) carrying most of the previously trapped sample gas with it. The flow-controlling valve 72 is closed by the data acquisition and control unit 8 (see Fig. 1) when the desired charge of gas is present in the isotope ratio analyzer 24 (see Fig. 1). Then, the data acquisition and control unit 8 (see Fig. 1) initiates an isotope measurement of the CO<sub>2</sub> in the isotope ratio analyzer 24 (see Fig. 1). Again, measurement data generated by the IRGA 4 and isotope ratio analyzer 24 is acquired and stored or transmitted by the data acquisition unit 8. The whole sequence of events can be repeated either immediately, or after a delay period as dictated by the program loaded into the data acquisition unit 8.

The operation of a preferred embodiment of the cryogenic trap apparatus 82 shown in Fig. 5 (together with the sample conditioning unit 18 of Fig. 4), is as follows. With the liquid nitrogen dewar 112 filled to approximately 75% capacity, the data acquisition and control unit 8 (see Fig. 1) can control the temperature conditions of 'U' tube 108, in order to either cryogenically trap a gas sample which is condensable at liquid nitrogen temperatures, or thaw a previously trapped sample.

Under the control of the data acquisition and control unit 8 (see Fig. 1), when a sample is to be trapped, solenoid valve 102 is opened and no current is passed through the resistance heater wire 106. This action allows any nitrogen gas or air trapped in the upper part of cylinder 110 to escape through vent tube 100, through solenoid valve 102, and out of exhaust tube 104. The gas escaping from the upper part of cylinder 110, in turn allows the liquid nitrogen level in the cylinder 110 to rise to the same level as that of the dewar 112, thus immersing the lower part of 'U' tube 108 in liquid nitrogen. As long as these conditions exist,

the 'U' tube 108 will remain at liquid nitrogen temperatures and any gas flow through the interior of the 'U' tube 108 will condense if it is condensable at liquid nitrogen temperatures. When a sample is to be thawed or when the non-trapping state is required, the data acquisition and control unit 8 (see Fig. 1) closes solenoid valve 102 and applies power to the resistance heater wire 106. The current passing through the resistance heater wire generates heat and starts to evaporate nearby liquid nitrogen. The nitrogen gas thus generated cannot escape from the upper part of the cylinder 110 since solenoid valve 102 is closed and the result is that the liquid nitrogen level inside the cylinder 110 is pushed down below that of the dewar 112. The liquid nitrogen level inside the cylinder 110 continues to be pushed down by the nitrogen gas until it is close to the bottom edge of the cylinder 110. As long as solenoid valve 102 remains closed and current passes through resistance heater wire 106, the liquid nitrogen level inside the cylinder 110 will remain below the 'U' tube 108. The heat generated by the resistance heater wire continues to heat the 'U' tube 108, providing enough energy to evolve any gases previously trapped in the interior of the 'U' tube 108. The power applied to the resistance heater wire 106 by the data acquisition and control unit 8 (see Fig. 1) can be modulated in order not raise the temperature of the 'U' tube 108 so high that it radiates excessive heat and boils liquid nitrogen unnecessarily.

Although the description above contains many specificities and utilizes the specific example of analyzing CO<sub>2</sub> in air, this should not be construed as limiting the scope of the invention but as merely providing illustration of this invention with respect to particular gases.

In further embodiments of the invention, the sample gas mixture can be provided liquid or solid samples. The solid and liquid samples are turned into a gas via heating or through combustion. The sample gas mixture can be provided from any one of a number of commercially available devices capable of generating gases from non-gaseous samples in order to facilitate gas concentration or gas isotope ratio measurements. For example, a Dumas combustion device such as the one manufactured by Fisons Instruments, Inc. of Beverly, Massachusetts 01915, could be connected to the gas inlet of the present invention and the gas mixtures generated from the combustion of solid sample materials analyzed in a similar

fashion to those previously described.

Thus, it should be understood that other embodiments could be created with variations in function, method and implementation. Although the present invention has been described in detail with reference only to present preferred embodiments, 5 it will be appreciated by one of ordinary skill in the art that various modifications can be made without departing from the invention. Accordingly, the scope of the invention should be determined by the appended claims and their legal equivalents.

We claim:



- 1        1.        A method for providing measurements of concentration and isotope ratio of a  
2        component in a sample gas mixture, comprising the steps of:  
3                loading said sample gas mixture into an instrument capable of measuring gas  
4        concentration;  
5                loading said sample gas mixture into an instrument capable of measuring gas  
6        isotope ratio; and  
7                performing measurements of gas concentration and gas isotope ratio on said  
8        sample gas mixture.  
9
- 10       2.        The method for providing measurements of concentration and isotope ratio of  
11       a component in a gas mixture as set forth in claim 1, further comprising a step of  
12       conditioning said sample gas mixture.  
13
- 14       3.        The method for providing measurements of concentration and isotope ratio of  
15       a component in a gas mixture as set forth in claim 2, wherein said conditioning step  
16       occurs prior to said step of loading said sample gas mixture into said instrument  
17       capable of measuring gas isotope ratio.  
18
- 19       4.        The method for providing measurements of concentration and isotope ratio of  
20       a component in a gas mixture as set forth in claim 3, wherein said conditioning step  
21       includes a step of removing an interfering species from said gas mixture.  
22
- 23       5.        The method for providing measurements of concentration and isotope ratio of  
24       a component in a gas mixture as set forth in claim 4, wherein said removal of an  
25       interfering species step includes a step of passing said gas mixture through a chemical  
26       scrubber to remove said interfering species.  
27
- 28       6.        The method for providing measurements of concentration and isotope ratio of  
29       a component in a sample gas mixture as set forth in claim 4, wherein said component  
30       of said sample gas mixture is carbon dioxide and said interfering gas species is  
31       oxygen.  
32

1       7.     The method for providing measurements of concentration and isotope ratio of  
2     a component in a gas mixture as set forth in claim 3, wherein said conditioning step  
3     includes a step of increasing the concentration of said component of said sample gas  
4     mixture in order to improve the precision of said measurements.

5  
6       8.     The method for providing measurements of concentration and isotope ratio of  
7     a component in a gas mixture as set forth in claim 7, wherein said concentration  
8     increasing step includes a step of passing said sample gas mixture through a selective  
9     gas membrane.

10  
11      9.     The method for providing measurements of concentration and isotope ratio of  
12     a component in a gas mixture as set forth in claim 7, wherein said concentration  
13     increasing step includes a step of passing said sample gas mixture through a cryogenic  
14     trap.

15  
16      10.    The method for providing measurements of concentration and isotope ratio of  
17     a component in a gas mixture as set forth in claim 7, wherein said concentration  
18     increasing step includes a step of introducing a carrier gas to said sample gas mixture.

19  
20      11.    The method for providing measurements of concentration and isotope ratio of  
21     a component in a gas mixture as set forth in claim 1, wherein said measurement of gas  
22     concentration and said measurement of gas isotope ratio is performed substantially  
23     simultaneously.

24  
25      12.    The method for providing measurements of concentration and isotope ratio of  
26     a component in a gas mixture as set forth in claim 1, further comprising a step of  
27     collecting said measurements of gas concentration and gas isotope ratio with a data  
28     acquisition and control unit.

29  
30      13.    The method for providing measurements of concentration and isotope ratio of  
31     a component in a gas mixture as set forth in claim 12, further comprising a step of  
32     transmitting said measurements of gas concentration and gas isotope ratio from said

1 data acquisition and control unit to a control center.

2

3 14. The method for providing measurements of concentration and isotope ratio of  
4 a component in a gas mixture as set forth in claim 1, wherein said instrument capable  
5 of measuring gas concentration and said instrument capable of measuring gas isotope  
6 ratio include a laser-based device.

7

8 15. An apparatus for providing measurements of concentration and isotope ratio  
9 of a component in a sample gas mixture comprising:

10 a device for measuring concentration of said component in said sample gas  
11 mixture;

12 a device for measuring isotope ratio of said component in said sample gas  
13 mixture;

14 a means to load said sample gas mixture into said concentration measuring  
15 device and into said isotope ratio measuring device.

16

17 16. The apparatus for providing measurements of concentration and isotope ratio  
18 in a component of a sample gas mixture as set forth in claim 15, wherein said isotope  
19 ratio measuring device is a laser-based device.

20

21 17. The apparatus for providing measurements of concentration and isotope ratio  
22 of a component in a sample gas mixture as set forth in claim 16, wherein said  
23 concentration measuring device is an infrared gas analyzer.

24

25 18. The apparatus for providing measurements of concentration and isotope ratio  
26 of a component in a sample gas mixture as set forth in claim 16, wherein said  
27 concentration measuring device is a laser-based device.

28

29 19. The apparatus for providing measurements of concentration and isotope ratio  
30 of a component in a sample gas mixture as set forth in claim 15, wherein said loading  
31 means comprises a pump coupled to said concentration measuring device and to said  
32 isotope ratio measuring device.

1     20.     The apparatus for providing measurements of concentration and isotope ratio  
2     of a component in a sample gas mixture as set forth in claim 15, further comprising a  
3     sample conditioning unit that conditions the sample gas mixture prior to introduction  
4     to the laser-based device.

5  
6     21.     The apparatus for providing measurements of concentration and isotope ratio  
7     of a component in a sample gas mixture as set forth in claim 20, wherein said sample  
8     conditioning unit includes a chemical scrubber to remove an interfering gas species  
9     from said sample gas mixture.

10  
11     22.     The apparatus for providing measurements of concentration and isotope ratio  
12     of a component in a sample gas mixture as set forth in claim 21, wherein said  
13     component of said sample gas mixture is carbon dioxide and said interfering gas  
14     species is oxygen.

15  
16     23.     The apparatus for providing measurements of concentration and isotope ratio  
17     of a component in a sample gas mixture as set forth in claim 20, wherein said sample  
18     conditioning unit includes a selective gas membrane to remove an interfering gas  
19     species from said sample gas mixture.

20  
21     24.     The apparatus for providing measurements of concentration and isotope ratio  
22     of a component in a sample gas mixture as set forth in claim 20, wherein said sample  
23     conditioning unit includes a cryogenic trap to remove an interfering gas species from  
24     said sample gas mixture.

25  
26     25.     The apparatus for providing measurements of concentration and isotope ratio  
27     of a component in a sample gas mixture as set forth in claim 15, further comprising a  
28     means for increasing the concentration of said component of said sample gas mixture  
29     in order to improve the precision of said measurements.

30  
31     26.     The apparatus for providing measurements of concentration and isotope ratio  
32     of a component in a sample gas mixture as set forth in claim 25, wherein said means

1 for increasing the concentration of said component of said sample gas mixture  
2 comprises a gas selective membrane.

3

4 27. The apparatus for providing simultaneous measurements of concentration and  
5 isotope ratio of a component in a sample gas mixture as set forth in claim 25, wherein  
6 said means for increasing the concentration of said component of said sample gas  
7 mixture comprises a cryogenic trap.

8

9 28. An apparatus for providing measurements of concentration and isotope ratio  
10 of a component in a sample gas mixture comprising:

11 a gas concentration analyzer;

12 an isotope ratio analyzer;

13 a sample conditioning unit coupled to the isotope ratio analyzer and the gas  
14 concentration analyzer;

15 a pump coupled to the isotope ratio analyzer for drawing the sample gas  
16 mixture into the apparatus; and

17 a data acquisition and control unit coupled to at least one of the gas  
18 concentration analyzer, the isotope ratio analyzer, the sample conditioning unit and  
19 the pump for controlling operation of the apparatus.

20

21 29. The apparatus for providing measurements of concentration and isotope ratio  
22 of a component in a sample gas mixture as set forth in claim 28, wherein a laser based  
23 device comprises the gas concentration analyzer and the isotope ratio analyzer.

1/4

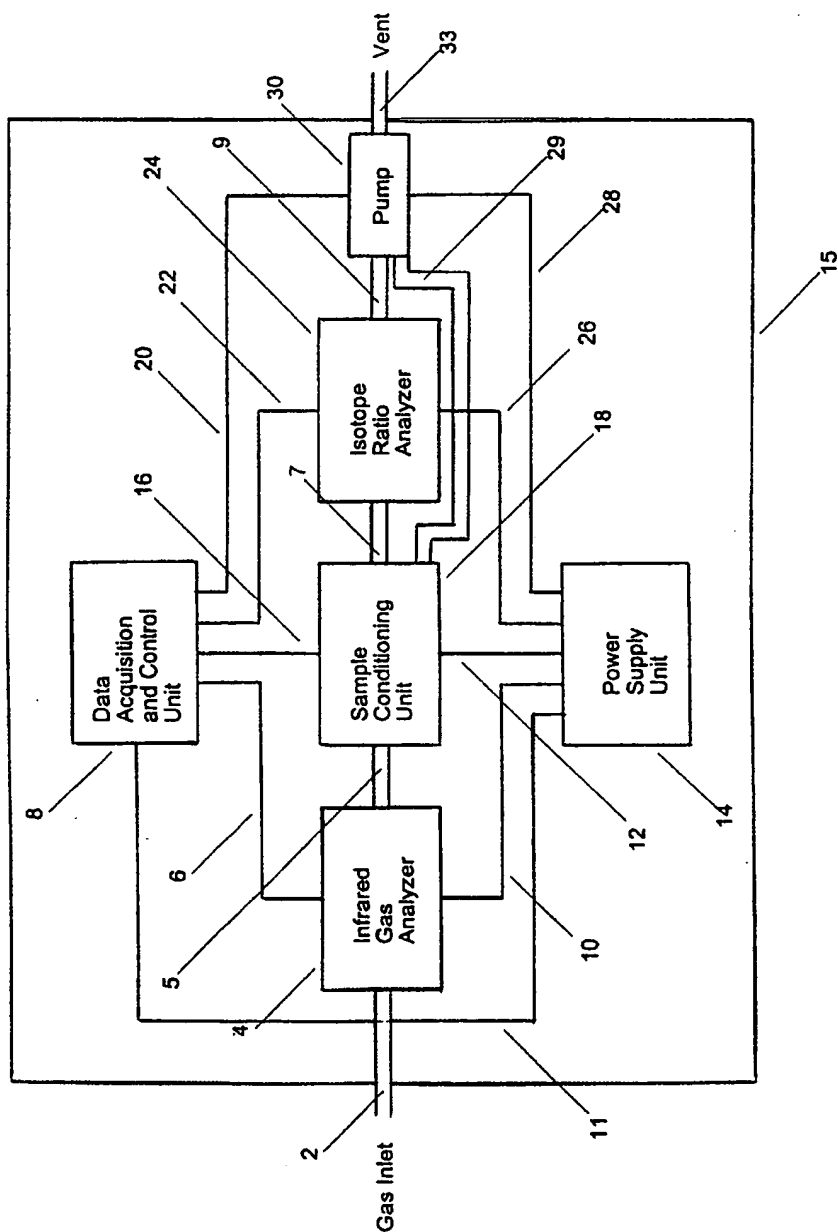


Fig. 1

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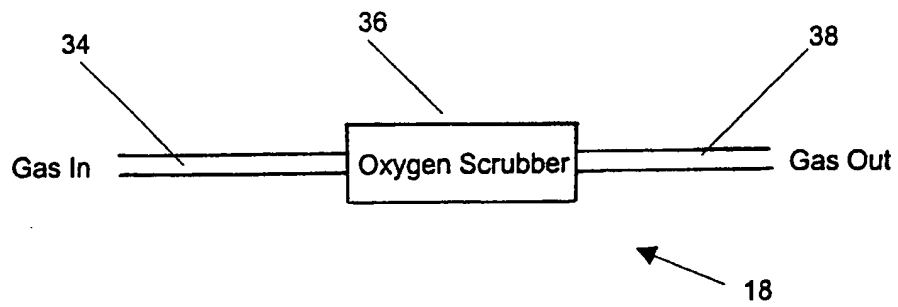


Fig. 2

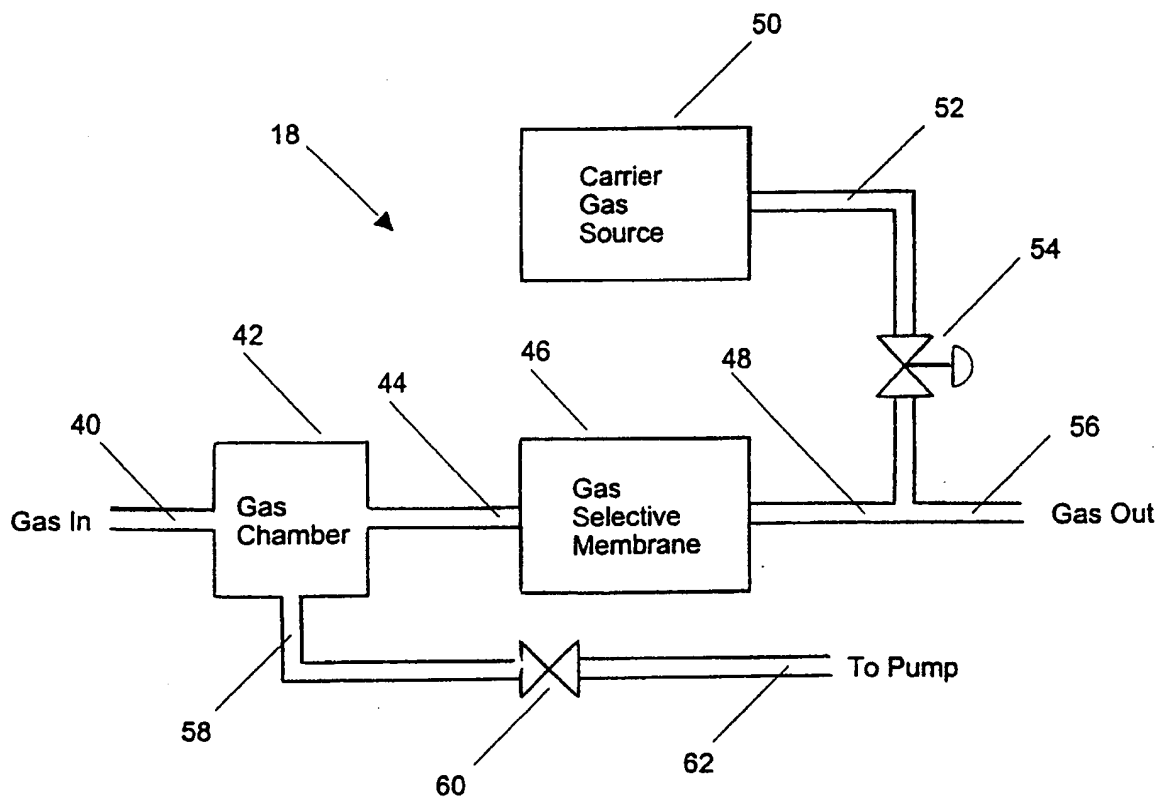


Fig. 3

3/4

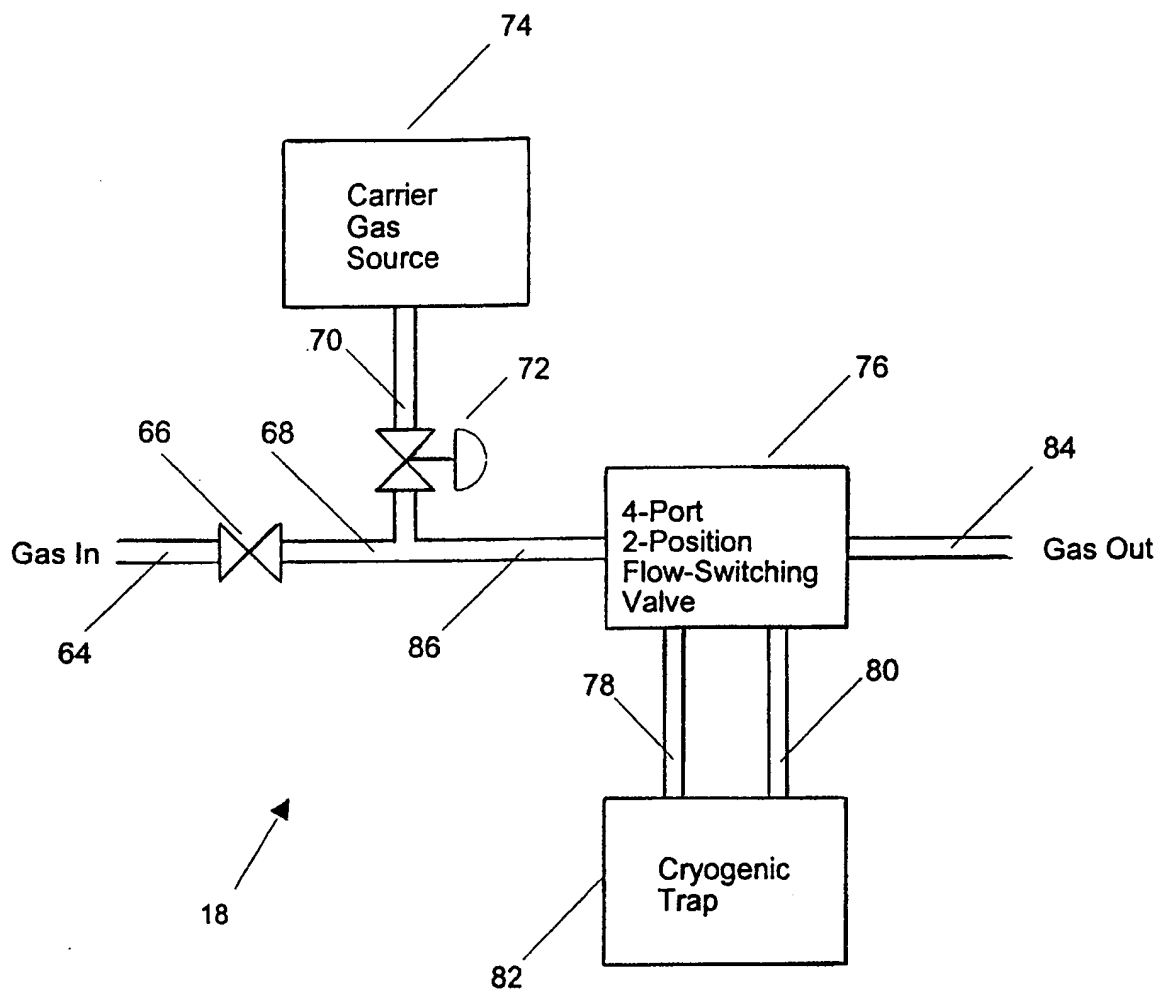


Fig. 4



4 / 4

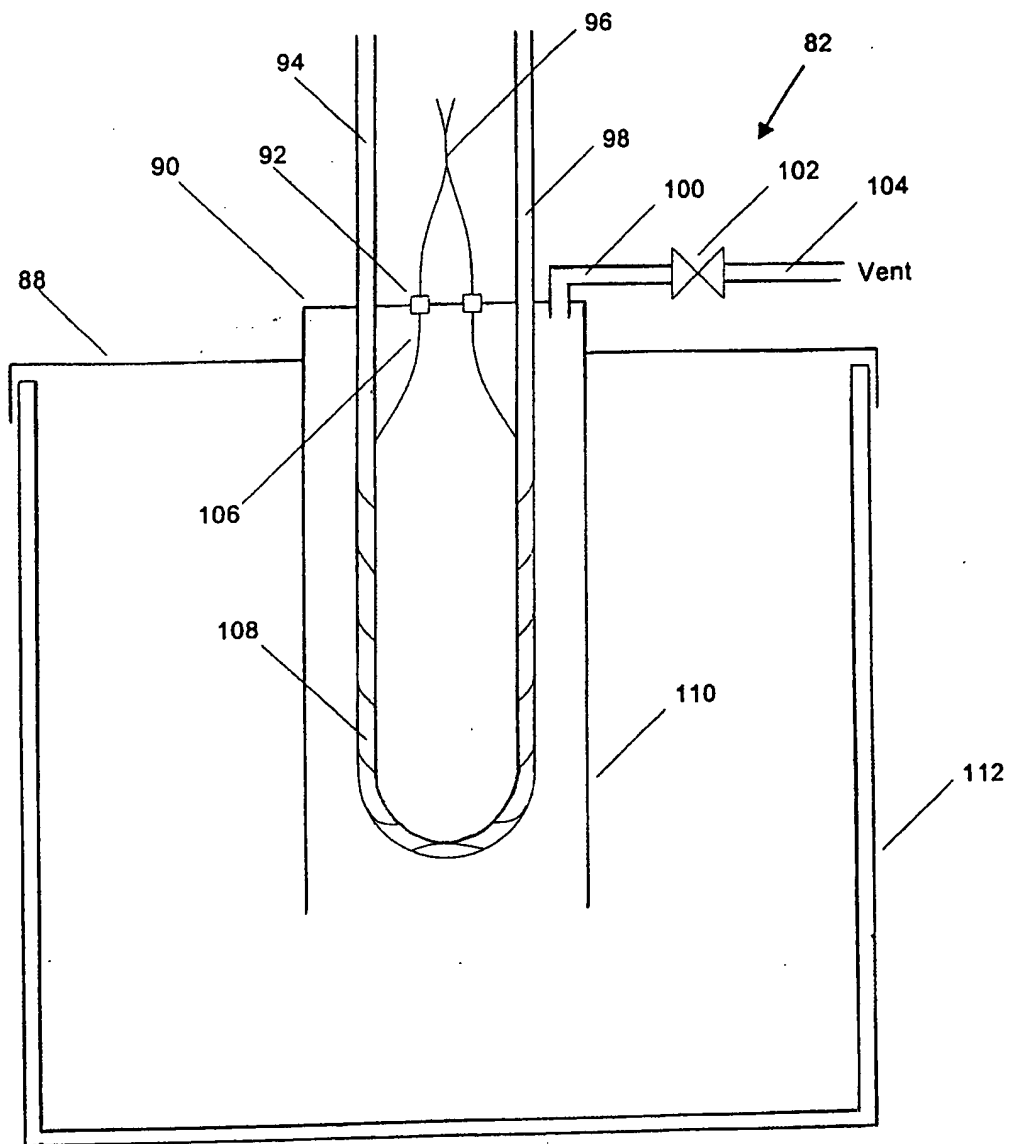


Fig. 5

# INTERNATIONAL SEARCH REPORT

Intern. Application No  
PCT/US 99/03755

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G01N21/35 G01N33/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 317 156 A (COOPER DAVID E ET AL) 31 May 1994	1,11-19
Y	see column 4, line 47 - column 5, line 36; figures 2,3,7	2-9, 20-29
Y	US 4 902 896 A (FERTIG SR GLENN H ET AL) 20 February 1990  see column 5, line 41 - line 49	2-7, 20-22, 25,28,29
Y	EP 0 819 937 A (UNIV NOTTINGHAM) 21 January 1998 see column 1, line 2 - line 3 see column 1, line 48 - line 54 see column 2, line 14 - line 19  -/--	2,3,7-9, 20,23-29

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 May 1999

Date of mailing of the international search report

01/06/1999

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Scheu, M

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/03755

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 5 838 008 A (ESLER MICHAEL BRIAN ET AL) 17 November 1998 see claims 15,18,21 ---	1,15
L	LICOR GAS ANALYZER: LI-6251, XP002103275 Retrieved from Internet: <url: http://env.licor.com/products/gasAnalyzers/6251.htm> 20 May 1999 see the whole document http://env.licor.com/products/analyzer.htm ---	
L	LASER-ASSISTED RATIO ANALYZER (LARA), XP002103276 Retrieved from Internet: <url: http://www.phy.uab.edu/exobiology/lara.htm 1> 20 May 1999 see the whole document -----	

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